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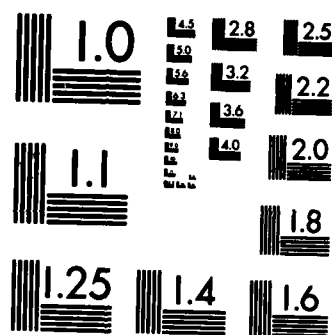
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Fuel Sediment Analysis by ESCA

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*Combustion and Fuels Branch
Chemistry Division*

February 25, 1983



NAVAL RESEARCH LABORATORY
Washington, D.C.

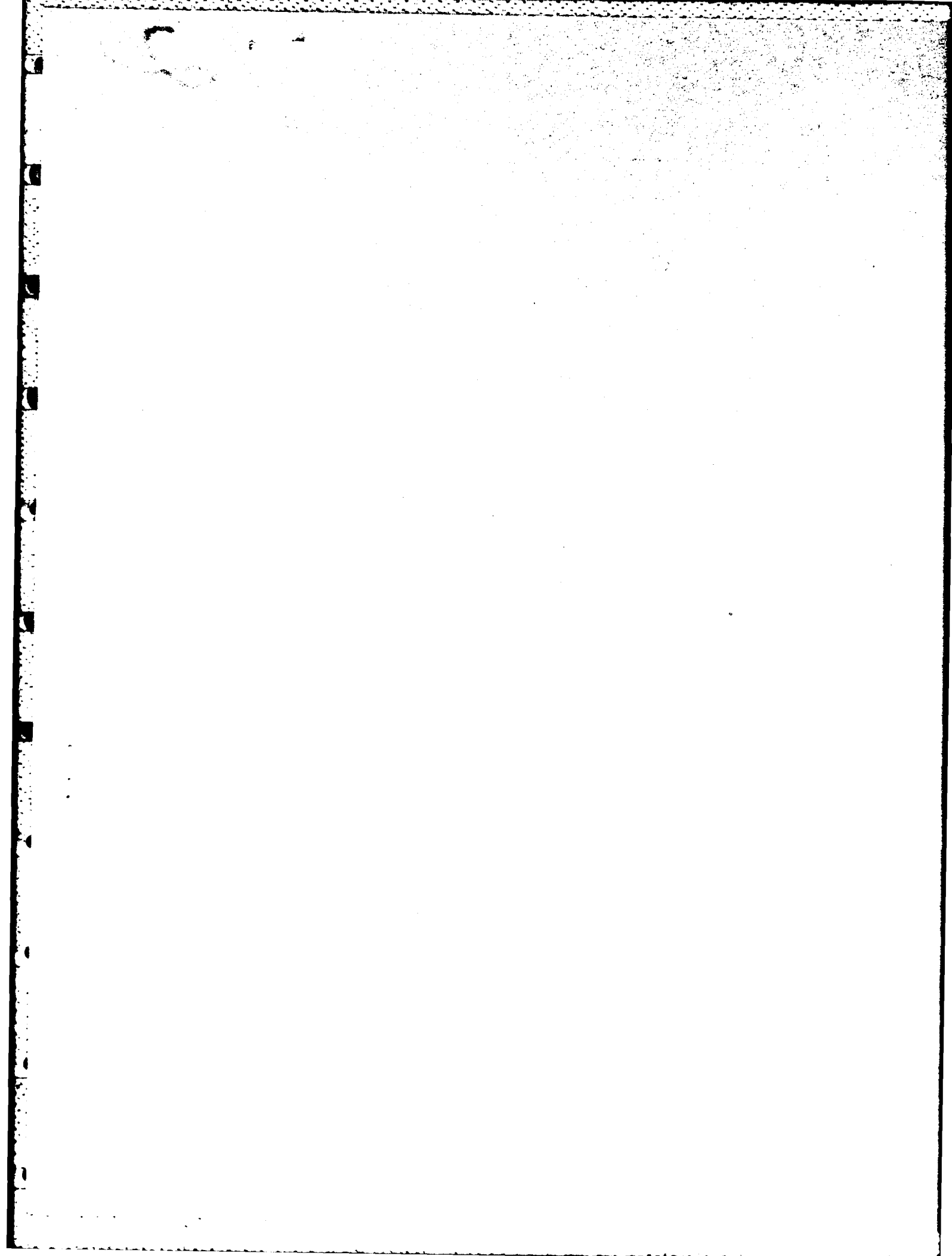
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The technique of x-ray photoelectron spectroscopy (XPS, ESCA) was applied to the analysis of sediments which are formed in fuel and which degrade fuel storage stability. Samples studied included sediments formed in a Navy Paraho Shale II DFM fuel by doping fuel samples with 2,5-dimethylpyrrole and stressing the mixtures for periods of 4 to 28 days at 80°C. Several naturally occurring sediments were also investigated. Carbon, oxygen, nitrogen, and sulfur spectra were obtained where applicable.		

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20. ABSTRACT (Continued)

Atomic ratio results show indications of changes in sediment composition over time, and indicate that the composition of various fractions associated with a given sediment may differ. Comparisons of the ESCA spectra of induced vs natural sediments indicated some differences particularly in the nitrogen spectra.

Some solubility studies were performed to determine effects of stress time on solubility. The sediment fractions remaining after solvent treatment were also subjected to analysis by ESCA. A comparison of their spectra with the sediment spectra taken before solvent treatment indicated differences in the atom ratios. Structural feature comparisons were inconclusive.

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FUEL SEDIMENT ANALYSIS BY ESCA

INTRODUCTION

When stored for prolonged periods of time, fuels may degrade in quality through the formation of insoluble materials. Experimental evidence indicates that heteroatomic organic compounds, particularly ones containing nitrogen, promote sediment formation [1]. To date, there is considerable uncertainty regarding the structural units which comprise the sediment particles. Elucidation of the nitrogen, sulfur, and oxygen functionalities involved would significantly improve the understanding of the chemistry of fuel instability.

It has been suggested that x-ray photoelectron spectroscopy (XPS) is particularly useful in the definition of the structural features of materials containing light elements such as carbon, nitrogen, and oxygen [2]. Information regarding the chemical environment of elements such as oxygen and nitrogen can be derived from kinetic energy differences between their core electrons upon their ejection from the atom by X radiation. The kinetic energy of the ejected electron decreases as the electron binding energy increases [2] and vice versa. Since binding energies, even of inner-shell electrons, are affected by their chemical environment, it is certainly conceivable that energy shifts should be useful indicators of the moieties present.

Thus, XPS has been used in an attempt to determine oxygen and nitrogen moieties in various sediments; some of them produced by doping fuel samples with various pyrroles. In addition to the structural studies, some quantitative studies were undertaken.

SAMPLES

Fuel sediment samples studied in this work were derived principally from diesel fuel marine (DFM) refined from Para crude shale oil by Sohio. The sediments which were formed by doping fuel with various pyrroles were derived from sample D-1 a Shale II fuel which has been well characterized [3]. Other sediments included several formed in undoped Shale II preacid DFM (a composite sample taken before the final refining step), and in Shale I, DFM.

Two model compounds selected for their stability in vacuo and for their oxygen/nitrogen functionalities, trans-dibenzoyl ethylene and melatonin (N-acetyl-5-methoxytryptamine), were also analyzed.

INSTRUMENTATION

The spectrometer used in this study was a McPherson ESCA 36 photoelectron spectrometer equipped with an aluminum anode. The detector is a single channel multiplier.

EXPERIMENTAL WORK

ESCA Sample Preparation

Solid samples to be inserted in the sample chamber of the ESCA spectrometer were mounted on 1-cm x 2-cm aluminum planchets by manually scraping small amounts of the solids onto the planchet

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surface with the back of a flexible, stainless steel spatula. To facilitate sample adherence, the planchets were abraded with a coarse metal file and then etched in a concentrated solution of FeCl_3 . Samples thus prepared were mounted on the ESCA sample wheel which can accommodate up to 8 samples. Table 1 lists the samples examined in this work.

ESCA Analysis

All model compound and sediment samples studied were analyzed for carbon, oxygen, and, where applicable, nitrogen using the narrow-scan ESCA technique. Samples were irradiated with aluminum K x-rays (1486.6 eV). In some cases a sulfur energy region was also scanned. A typical narrow scan focused on the appropriate binding energy region of interest and was typically 18 to 20 eV wide. For carbon, nitrogen, and oxygen the core electrons were $1s$ electrons and the (elemental) binding energies were 284, 399 and 532 eV [2]. For sulfur studies, $2p$ electrons were used ($2p\ 1/2 = 165$ eV; $2p\ 3/2 = 164$ eV). A gold planchet was used as an energy standard. Gold has two generally well resolved binding energy peaks which correspond to the $4f_{7/2}$ and $4f_{5/2}$ electrons. Peak energies for these electrons are 83 and 87 eV. All peak energies were corrected to the lower energy gold peak.

ESCA spectra for single elements were typically composites of 5 to 50 individual scans. The number of scans was varied to accommodate differences in peak intensity arising from such factors as concentration and elemental sensitivity (or relative *ease of detection*). A typical scan consisted of 150 points with an energy difference of 0.12 eV between points. Point-to-point step time was 1 s. In general, for samples containing oxygen, carbon, and nitrogen, spectra were taken in that order. After analysis of an elemental series was completed, the sample wheel was automatically rotated to the next position desired.

During several of the ESCA runs, attempts were made to evaluate the buildup of carbon contamination on the samples. The carbon buildup results from within the system itself. It was evaluated by monitoring aluminum planchet blanks, which were cleaned prior to insertion in the sample chamber, for carbon activity.

Two experimental series were run to monitor the effect of the source radiation on sample composition.

Sediment Preparation

In addition to the model compounds studied and the sediment samples which were run on an *as received* basis, several *fresh* sediment samples were analyzed. These were prepared following closely the experimental procedures employed for fuel instability studies at NRL [3].

The *fresh* sediment samples are labeled "MW" in Table 1. The fuel used was Shale II D-1 (DFM): three samples were doped with 450 ppm (w/v) of 2, 5 dimethylpyrrole and stressed at 80°C for 4, 14, and 28 days. The one exception to the NRL stability procedure was that two aluminum planchets were vertically suspended in each sample flask. This permitted collection of a sample of the *adherent gum* which typically adheres to the inside surfaces of the sample flasks. The adherent gum is differentiated from the sediment, a solid which generally settles to the bottom of the flask. The sediment can be dislodged from the flask by rinsing and shaking with heptane and is then collected by filtration. The gum is a smooth deposit which coats the inside of the sample flask and does not loosen when rinsed with heptane.

Solubility Studies

Samples of the freshly prepared sediment samples were treated with gum solvent a 1:1:1 mixture of toluene, methanol and acetone. This step was included initially to remove any adherent gum which

Table 1 — Samples Included in ESCA Studies Project

Sample	Elements No. Runs	Scanned	Description*
M-1	2	C,O,N	Model compound — melatonin: C/O/N = 6.5/1/1
T-DBE	2	C,O	Model compound trans-dibenzoyl ethylene: CO = 8/1
MW 4-1	2	C,O,N	4 day 80° D-1/DMP sediment
MW 4-2	4	C,O,N	4 day sediment remaining after solvent treatment
MW 4-3	1	C,O,N	Adherent gum from 4 day sediment
MW 14-1	4	C,O,N	14 day 80° D-1/DMP sediment
MW 14-2	3	C,O,N	14 day sediment following solvent treatment
MW 14-3	1	C,O,N	Adherent gum from 14 day sediment
MW 28-1	1	C,O,N	28 day 80° D-1/DMP sediment
MW 28-2	1	C,O,N	28 day sediment following solvent treatment
MW 28-3	1	C,O,N	Adherent gum from 28 day sediment
D1-VI	1	C,O,N,S	14 day — 80° D-1/DMP "aged" lab sample
D1-VII	1	C,O,N	14 day — 80° D-1/CMP "aged" lab sample
D1-XXII	1	C,O,N	52 day — 43° D-1/DMP "aged" sample
D1-IV	1	C,O,N	14 day — 80° 2,4 DMP sediment
D1-LXII	1	C,O,N	14 day — 80° 1,3,5 trimethylpyrrole sediment
SHALE-II-VI	1	C,O,N,S	Shale II DFM (preacid), composite sediment stressed 14 days at 80°
SHALE I-F	2	C,O,N,S	"Fine" Shale I DFM sediment, second filtration (no stress)
SHALE I-C	1	C,O,N,S	"Coarse" Shale I DFM sediment, first filtration (no stress)
SHALE I - XXVII	1	C,O,N,S	Shale I DFM sediment (stressed 14 days at 80°)
Good-Hope	1	C,O,N,S	A petroleum-based fuel sediment (stressed 18 days at 80°)

*Stress temperatures for sediment formation are in °C. All pyrrole concentrations in doped fuels were at a 450 ppm nitrogen level (wt/vol).

might coat the sediment surface. This was necessary since ESCA is a surface technique and results are obtained only from the first few nanometers of sample surface.

Because a considerable fraction of the sediments dissolved in the gum solvent, quantitative measurements were made on the freshly prepared sediments with that solvent and with its components. Nonquantitative measurements were made on several other sediments.

Other Work

Mass spectrometry and HPLC techniques were used in attempts to characterize the solid sediments and the fraction which was soluble in gum solvent. Solid samples were placed in capillary tubes and inserted into the sample chamber of the mass spectrometer on the end of a probe. Some attempts were made to separate the soluble components with HPLC.

RESULTS

ESCA peaks for the fuel sediments tended to be quite broad and frequently asymmetric, suggesting multiple functionalities. The samples are believed to be rather complex chemically and the ESCA spectra are consistent with this concept. For instance, several oxygen and carbon moieties and possibly two or more nitrogen functionalities could account for the broad peaks found for most fuel sediments and gums.

Figures 1 through 5 depict some selected spectra of model compound and sediment samples which serve to illustrate the apparently complex chemical nature of the sediments. A comparison of spectral features and peak widths (full widths at half maximum, FWHM) provides some insight to the apparent number if not the type of functionalities present. The sediment spectra selected were derived from freshly prepared D-1/2,5-dimethylpyrrole solid samples and an adherent gum. Spectra derived from the model compounds used in this study are also included, as is an oxygen (1s) spectrum of Al_2O_3 . The O (1s) spectra of the standard or model compounds containing one functionality are narrower and more symmetric than is the O (1s) spectrum of N-acetyl-5-methoxy-tryptamine, which has two oxygen moieties. Other comparisons can be made between model compound spectra and spectra of doped sediment samples. In general, there is an observed peak broadening and, in some cases, a trend toward asymmetry with increasing structural complexity.

Most of the sediment samples, whether from doped or undoped experiments, exhibit complex-appearing ESCA spectra. However, carbon peaks do indicate that there are some differences between doped and undoped sediments. Further, there appear to be differences between the shapes of nitrogen peaks among the various DMP sediments and adherent gum samples.

It was difficult to determine whether most spectral energy shifts were actually structurally induced or whether they were caused by charging of the sample surface [4]. The magnitude of the shifts was sometimes observed to vary between duplicate analyses of the same sample material and between dissimilar samples.

The effect of radiation on the sample surface was evaluated by collecting elemental spectra on identical samples exposed to x-radiation for varying periods of time. Spectral features did not appear to change with time over the time intervals involved. The exposure intervals were representative of those used during typical runs.

Peak areas were corrected for their respective elemental sensitivities [5] and for the number of scans used to generate the peak.

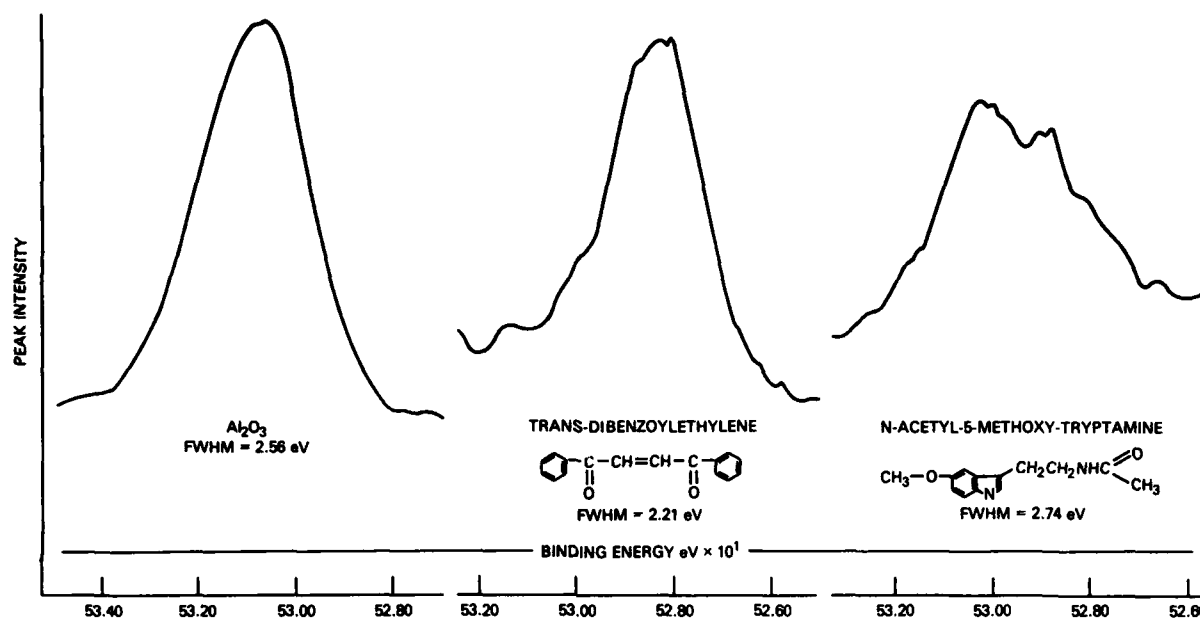


Fig. 1 — Oxygen (1s) ESCA peaks for standard or model compounds

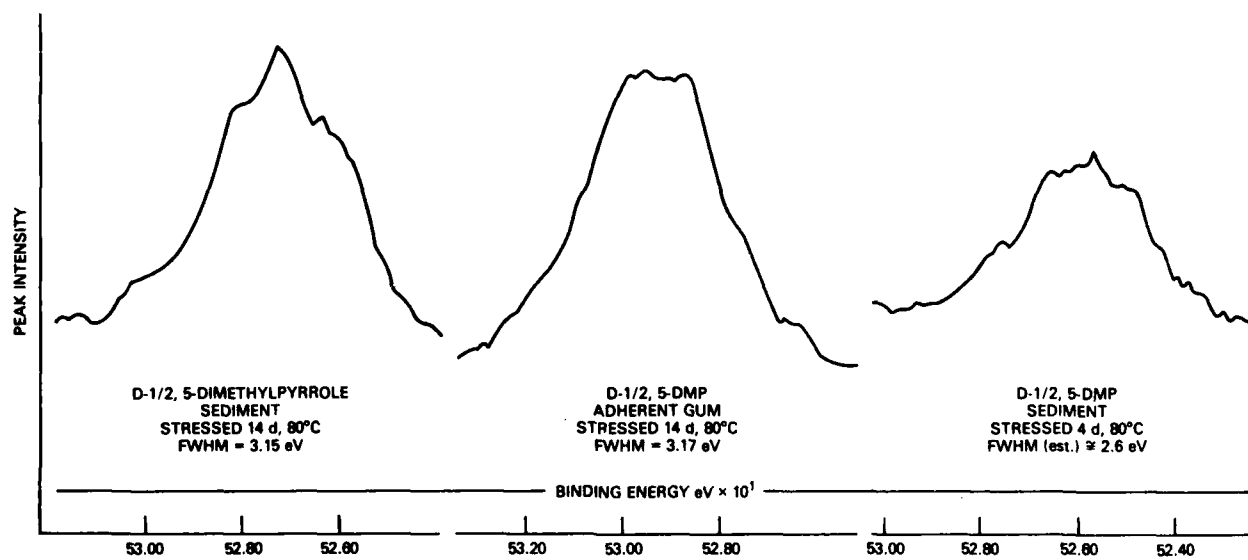


Fig. 2 — Oxygen (1s) ESCA peaks for representative sediment samples

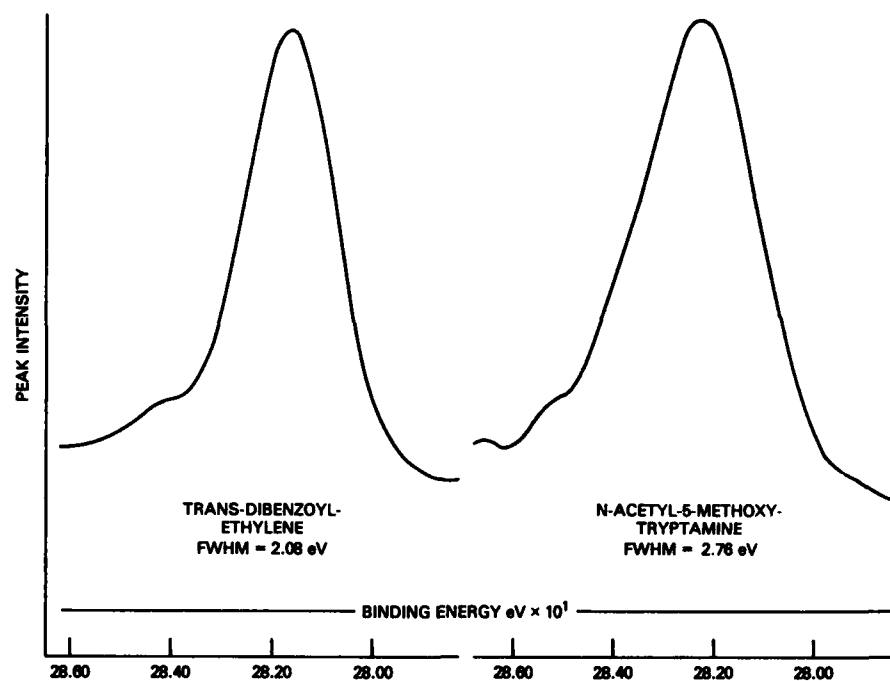


Fig. 3 — Carbon (1s) ESCA peaks for model compounds

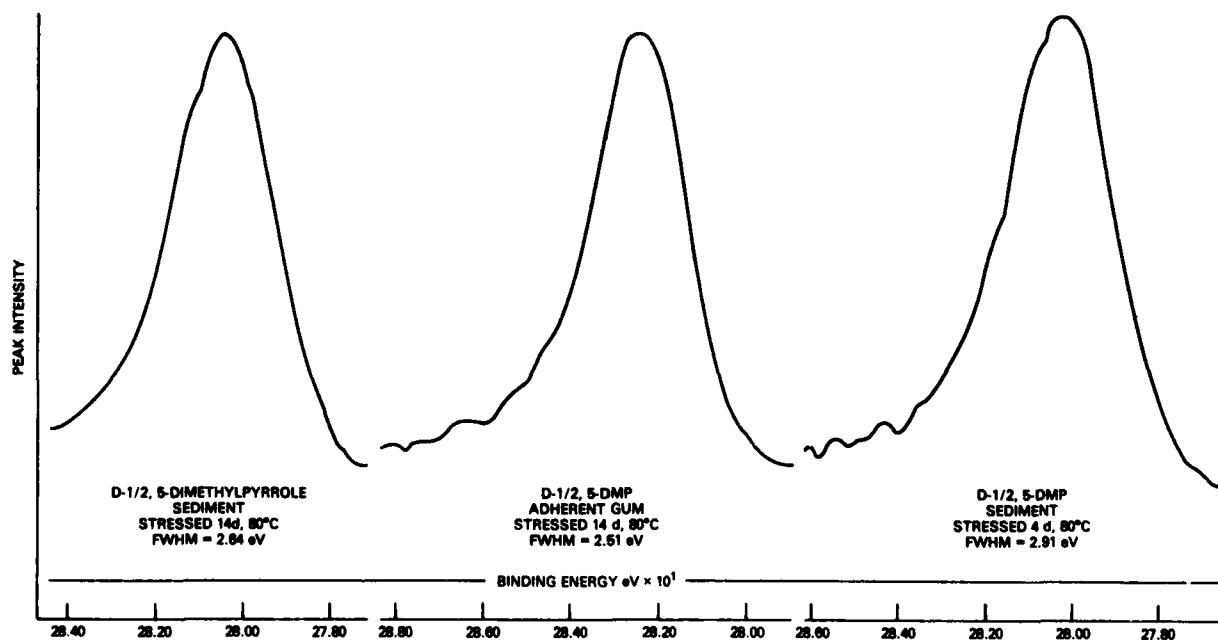


Fig. 4 — Carbon (1s) ESCA peaks for representative sediment samples

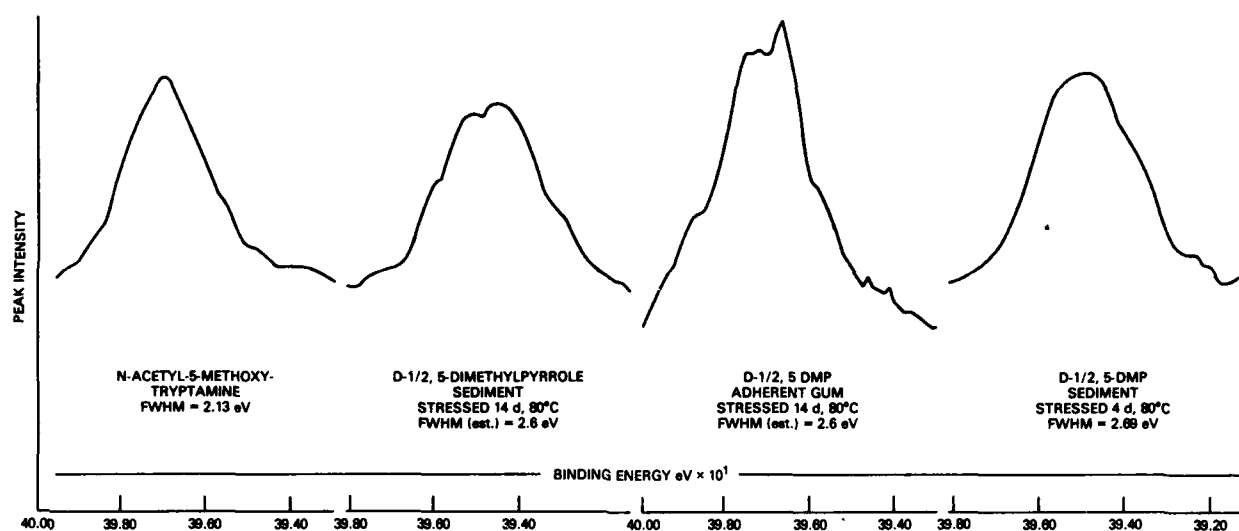


Fig. 5 — Nitrogen (1s) ESCA peaks for a model compound and for sediment samples

Carbon, oxygen, and nitrogen were typically determined. The carbon peaks were subject to background from carbon contamination or *adventitious* carbon [5]. Consequently, quantitative information regarding the carbon content of the samples is not included here.

Table 2 summarizes the O/N atomic ratios of various samples as determined by ESCA. Not included in the table are results from the analysis of the model compound melatonin. Duplicate ESCA elemental analysis for this pure compound were reproducible and yielded an O/N atomic ratio of 1:1.2. This contrasts with the 1:1 ratio expected from the known structure.

The 2,5-DMP sediments which were prepared for this study and analyzed shortly after their preparation (MW series) appear to have substantially lower O/N ratios than those from sediments which had been stored in the laboratory for a considerable time. Samples MW 4-1, 14-1, and 28-1, all *fresh* 80°C stress sediments, have ESCA O/N ratios which vary between 0.5 and 0.9. The *aged* samples, on the other hand, exhibited O/N ratios between 1.4 and 3.0 (samples D-1- VI, VII, and XXII in Table 2).

Figure 6 summarizes the results of the MW series. Note that the O/N ratios for both the *fresh* sediments and adherent gum fractions increase, apparently linearly, with stress time. Points representing the series of sediments which were the fractions insoluble in gum solvent are included on the graph but are not connected owing to the scatter. However, as the O/N ratio is roughly constant between the 4- and 14-day points (which are averages of 4 and 3 separate determinations), and as the large variation occurs in the 28-day point (one determination), it may be that the O/N ratio of this fraction is independent of stress time.

Referring to Table 2, note that the nitrogen values for the undoped fuel sediments are very low relative to all the doped sediment samples. The only exception is the Shale II (preacid) (VI) sample which is a product stream taken before the final step in the refining process.

Table 3 summarizes the results of the solubility studies. Clearly, stress time influences the solubility of the sediment samples; the solubility being greatest for samples stressed the shortest period of time. There is little difference between the solubility of the 14- and 28-day-stress samples.

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Table 2 — Summary of Sediment O/N Atomic Ratios
As Determined by ESCA

Sample	No. Determinations	Average O/N
MW 4-1	2	0.5 ± 0.14
MW 4-2	4	0.9 ± 0.07
MW 4-3	1	1.0
MW 14-1	4	0.7 ± 0.17
MW 14-2	3	1.1 ± 0.19
MW 14-3	1	1.4
MW 28-1	1	0.9
MW 28-2	1	0.6
MW 28-3	1	2.0
D1-VI	1	3.0
D1-VII	1	1.4
D1-XXII	1	1.4
D1-IV	1	1.1
D1-LXII	1	1.2
SHALE II-VI	1	0.9
SHALE I-F	2	*
SHALE I-C	1	$> 3.0^{**}$
SHALE I-XXVII	1	$\geq 3.0^{**}$

*Amount of nitrogen present was too small to calculate.

**Low nitrogen content, "order of magnitude" results at best.

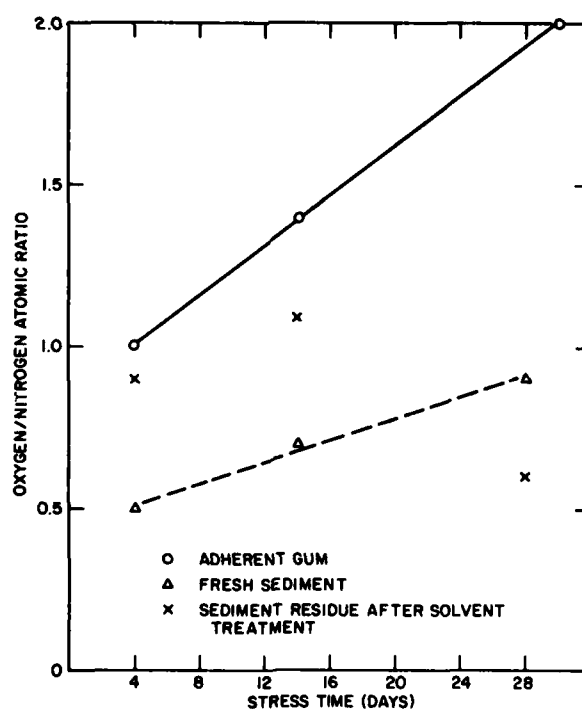


Fig. 6 — Oxygen/nitrogen atomic ratios for sediments and gums from 2, 5-dimethylpyrrole doped samples

Table 3 — Results of Sediment Solubility Studies

Sample	Description	Solvent	No. Weighings	Agitation	Weight Loss (%)
A-1	MW-4 day 80°	gum	1	ultrasonic	49.5
A-2	MW-14 day 80°	gum	1	ultrasonic	26.5
A-3	Lab 52 D-43°	gum	1	ultrasonic	15.0
B-1	MW-4 day 80°	gum	2	ultrasonic	58.8
B-2	MW-14 day 80°	gum	2	ultrasonic	26.4
C-1	MW-4 day 80°	gum	3	mechanical	58.8
C-2	MW-14 day 80°	gum	3	mechanical	29.9
D-1	MW-28 day 80°	gum	2	mechanical	33.0
D-2	MW-28 day 80°	acetone	2	mechanical	30.3
D-3	MW-28 day 80°	methanol	2	mechanical	15.6
E-1	MW-4 day 80°	methanol	2	mechanical	51.0
E-2	MW-4 day 80°	acetone	2	mechanical	30.3

As samples treated with pure toluene did not dissolve to any measurable degree, they are not included in Table 3. Since samples were soluble in methanol and acetone, as well as in gum solvent, the soluble fraction of the sediment is most probably somewhat polar.

It is interesting to observe that the solubilities of the 4- and 28-day materials in acetone were comparable, but that they were quite different in methanol. It is quite likely that the solubility comparisons are indicative of similarities and differences between the sediments.

Little effort was concentrated on the mass spectrometric studies. It was observed, however, that each sample introduced into the sample chamber released a small amount of volatiles even at ambient temperature under the vacuum conditions of the system (roughly 10^{-6} torr). When the probe was heated to 400°C, nothing else was observed to vaporize from the surface of the sample. A preliminary look at the mass peaks indicated some masses greater than 200 amu for the readily volatilized material.

SUMMARY AND CONCLUSIONS

ESCA and related studies on doped and undoped fuel sediments indicate that the sediment types differ somewhat from each other, particularly in regard to their nitrogen content. The results obtained during the course of this work further indicate that O/N ratios may be affected by sediment aging. An interesting point may be made if one compares the O/N ratio of sample MW 14-1 (0.7) with that of sample D-1-VII (1.4). Both are derived from doping Shale II DFM sample D-1 with 2,5 DMP at the 450 ppm of nitrogen level and stressing at 80°C for 14 days. The major difference between the 2 samples is that the first was freshly prepared whereas the second had been *aging* on a laboratory bench for some time. Coincidentally, the atomic ratio of 1.4:1 (O/N) corresponds to a weight ratio of 1.6:1, a figure apparently in line with other elemental analysis results.

Although analysis by ESCA is not typically so quantitative as some other methods, the atomic ratio results presented in this work certainly present evidence of trends in the DMP sediments which bear investigation. It seems reasonable to consider the effects of aging on analysis results and to consider what factors are important to the aging process.

The solubility studies suggest that further clues to the mechanism of sediment formation and elucidation of their structural components may be provided from solubility data and from analyses of the soluble and insoluble fractions.

Finally, the ESCA spectra obtained provided no clear-cut structural information, but did, in some cases, indicate similarities and differences between various sediments.

SUGGESTIONS FOR FUTURE WORK

ESCA Studies

Future studies involving ESCA should focus initially on sample preparation, effects of carbon contamination and charging and, most importantly, resolution of complex spectra into individual components with subsequent assignment of resolved peaks to functional groups. Other investigations should center on a feasibility study of the potential utility of a combination of XPS and ultraviolet photoelectron spectroscopy (UPS). It is possible that an instrument located elsewhere might be involved initially in the feasibility study.

Sediment Characterization

During the course of this investigation a number of questions have arisen, which, when answered, might provide valuable clues to the mechanism of sediment formation and to the general chemical structure of those materials. Accordingly, the following is a list of recommendations for future sediment characterization studies.

- Perform more studies to determine the solubility properties of various kinds of sediments. Characterize the soluble fractions.
- Characterize the volatile fraction which pumps off under low vacuum.
- Ascertain the effects of aging (in the absence and presence of light) on the elemental ratios; consider temperature stressing of the sediments during the drying process.
- Ascertain the role of the fuel in sediment formation after doping with DMP and other materials; consider using other liquids to grow sediments.
- Look at the solid sediment surface with mass spectrometric techniques.
- Compare properties of doped and undoped sediment samples.
- Look at sediment particles after solvent treatment.
- Use light scattering to compare molecular weights of sediments and solvent treated vs nontreated samples.
- Define molecular weights of sediments prepared or treated in various ways.

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